

Electrical Characteristics of Barium Strontium Titanate-Oxide Composite Films

S. Sengupta, L.C. Sengupta, S. Stowell, D.P. Vijay, and S.B. Desu

ARL-TR-681

December 1994



DTIC QUALITY INSPECTED 3

19950124 008

Approved for public release; distribution unlimited.

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the Collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information including successions for reducing this burden. Washington Headquarters Services. Directorate for Information Operations and Reports, 12/5 Jefferson

. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
-	December 1994	
TITLE AND SUBTITLE Electrical Characterist Titanate-Oxide Composit AUTHOR(S) S. Sengupta, L.C. Sengu	e Films	i um
*D.P. Vijay, and *S.B.		
Army Research Laborator Watertown, MA 02172-00 AMSRL-MA-CA	y	8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-681
SPONSORING/MONITORING AGENCY NAME(S) A	ND ADDRESS(ES)	10. SPONSORING/MONITORING AGENCY REPORT NUMBER
*D.P. Vijay and S.B. De Virginia Tech, Blacksb	su, Dept. of Materia urg, VA 24061	ls Science and Engineering,
Approved for public rel	ease; distribution u	
ceramics have been formule be tailored for use in various antennas and insertion has accommodate the frequer composites have been fab The electrical properties,	alated and have demonstrated ad- ous electronic devices. One applia s been accomplished into several acces required by these phased am	excimer laser as an ablation source. and the tunability (change in the

Unclassified NSN 7540-01-280-5500

17. SECURITY CLASSIFICATION OF REPORT

14. SUBJECT TERMS

Ferroelectric Film

15. NUMBER OF PAGES

20. LIMITATION OF ABSTRACT

16. PRICE CODE

19. SECURITY CLASSIFICATION OF ABSTRACT

Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE

Unclassified

Contents

		Page
Int	roduction	ı
Ex	perimental	1
Re	esults and Discussion	
	Electronic Measurements	. 2
Co	onclusions	. 4
Ac	knowledgements	. 4
Re	ferences	4
	Figures	
1.	Capacitance versus voltage for BSTO (undoped) deposited on	2
	RuO ₂ /Sapphire with Pt top electrode	3
2.	Capacitance versus voltage for BSTO/1 wt% Oxide II deposited on RuO ₂ /Sapphire with Pt top electrode	. 3
	Tables	
1.	Electronic Properties of BSTO (Ba = .6) and BSTO/Oxide Composite Thin Films	4

Acces	sion For	1
NTIS	GRA&I	W.
DTIC	TAB	
Unana	oume#d	
Just 1	fication_	
By Dist _e r	ibution.	
Avai	lability	Codes
	Avail and	/or
Diet.	Special	
11		
h,		

INTRODU€TION

Phased array antennas are currently constructed using ferrite phase shifting elements. These antennas can steer transmitted or received signals either linearly or in two dimensions without mechanically oscillating the antenna. Due to the circuit requirements necessary to operate these present day antennas, however, these are costly, large and heavy. Therefore, the use of these antennas has been limited primarily to military applications which are strategically dependent on such capabilities. In order to make these devices available for many other commercial and military uses, the basic concept of the antenna must be improved. Towards this goal, a ceramic Barium Strontium Titanate, Ba_{1-x}Sr_xTiO₃, (BSTO), phase shifter using a planar microstrip construction has been demonstrated. However, to meet the required performance specifications (e.g., maximum phase shifting ability), the BSTO electronic properties must be optimized. As part of this optimization process, various composites of BSTO and non-ferroelectric oxides have been formulated and proven successful.

However, in order to obtain higher operating frequencies (30 GHz and beyond) and to decrease the voltage requirements, thin film fabrication of the above candidate materials is necessary. This paper outlines the work on the characterization of the thin films of undoped and modified BSTO deposited by the pulsed laser deposition (PLD) method. The electronic properties of the films were measured using an HP 4194A impedance analyzer. The results of these measurements will be discussed.

EXPERIMENTAL

The metallized films used for the electrical measurements were: (1) Sapphire / RuO₂ /BSTO / Pt and (2) Sapphire / RuO₂ /BSTO with 1 wt.% oxide II / Pt. Prior to PLD, the sapphire substrates utilized underwent a cleaning cycle which included an ultrasonic cycle of TCE followed by two methanol ultrasonic cycles. The samples were then rinsed with methanol and air dried. The lattice parameters and dielectric constants of the sapphire substrates used in this experiment are 4.76 Å and 11 (at 300 K) respectively.

Prior to the thin film deposition, a ground plane electrode of Ruthenium oxide (RuO₂) was sputtered onto the substrates at a substrate temperature of 200 0 C and a O₂/Ar ratio of 1:4 with a total pressure of 10 mT. The Ruthenium oxide films were 3000 Å thick. The resistivity of the as-deposited films were in the order of 160 μ ohms-cm. They were annealed at 600 0 C for 30 minutes to lower the resistivity and were cooled by furnace quenching. The resistivity of the annealed films were measured to be 110 μ ohms-cm.

The targets chosen for this work were Ba_{0.6}Sr_{0.4}TiO₃ (BSTO) and BSTO with 1 wt.% of an additive oxide, referred to hereafter as oxide II. The PLD of the ferroelectric thin films was accomplished using a Questek 2000 krypton-fluoride excimer laser with a wavelength of 248 nm and a repetition rate of 10 Hz. The substrate was held parallel to the target and their separation distance was maintained at 55 mm. The average pulse energy was 300 mJ with a 20 ns pulse width. The oxygen partial pressure in the chamber was 100 mT and the substrate temperature was 500 °C, which was monitored by a thermocouple clamped between the heater and the substrate. The powder pressed ceramic targets were prepared according to a description

published previously. ² A Dektak-200 profilometer was used to measure the films thicknesses. It was measured to be 6000 Å for both the films. The compositions of the films were confirmed by Glancing Angle X-ray-diffraction (GAXRD).

After the deposition of the thin films, the top Pt electrodes were deposited by electron beam evaporation. The thicknesses of the top electrodes were measured to be approximately $3000~\text{\AA}$ using a Dektak-200 profilometer.

The dielectric constant (ϵ ') and % tunability were determined for both thin film/substrate combinations. The % tunability of a material is determined using the following equation:

% tunability = {
$$\varepsilon'(0) - \varepsilon'(Vapp)$$
}/ { $\varepsilon'(0)$ } (1)

The tunability measurements were taken with an applied electric field which ranged from 0 to \pm 3.3 V/micron (μ m). The electronic properties were measured at two frequencies, 30 KHz and 0.5 MHz. Capacitance versus voltage (C-V) measurements for the films were taken using an HP4194 impedance / phase gain analyzer. The voltage, applied internally through the HP 4194A, was varied from -2.0 V to +2.0 V.

RESULTS AND DISCUSSION

Electronic Measurements

Fig. 1 shows the capacitance versus voltage characteristics at 30 KHz for the BSTO (undoped) film deposited on RuO₂/sapphire. The curve shows a symmetric capacitance-voltage relationship which is characteristic of *paraelectric* films. The dielectric constant at zero bias was calculated to be 1380 and the tunability is 48% at a field of 3.3 V/μm. The bulk undoped material has a dielectric constant of 3300 and a tunability of 20% at 0.73 V/μm. It has been previously shown that the dielectric constant of ferroelectric films are inherently less than the bulk ceramic values due to oxygen defects at the electrode/film interface. Also any porosity and/or leakage current in the films will tend to decrease the dielectric constants obtained.

The C-V curve at 30 KHz for the BSTO/1 wt% oxide II film deposited on RuO_2 /sapphire is shown in Fig. 2. The curve shows a typical paraelectric behavior (i.e., a symmetric capacitance) with positive and negative bias applied. The dielectric constant at zero voltage calculated from this curve is 600. The tunability obtained up to 3.3 V/ μ m was 34%. The value for the dielectric constant found in the bulk ceramic target of BSTO/1 wt% oxide II was 2700 and a tunability of 46% at 2.5V/ μ m [1]. Table I summarizes the values of the dielectric constants and tunability of the various BSTO thin films measured at 30 KHz and their ceramic counterparts.

Similar measurements of the same thin films were also carried out at 0.5 MHz. For the undoped BSTO thin film, a dielectric constant of 940 and a tunability of 55% ($V_{applied} = 3.3 \text{ V/}\mu\text{m}$) were obtained. For the BSTO/oxide II thin film, a dielectric constant of 310 and a tunability of 39% ($V_{applied} = 2.0 \text{ V/}\mu\text{m}$) were obtained.

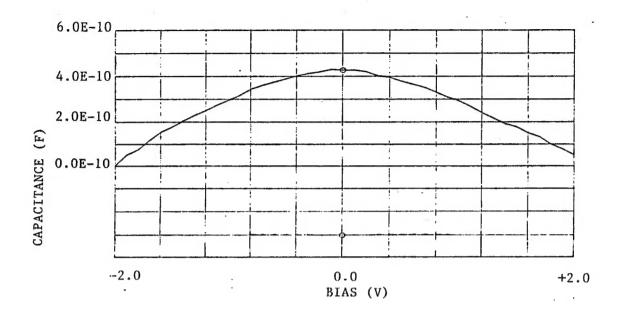


Fig. 1. Capacitance versus voltage for BSTO (undoped) deposited on RuO₂/Sapphire with Pt top electrode.

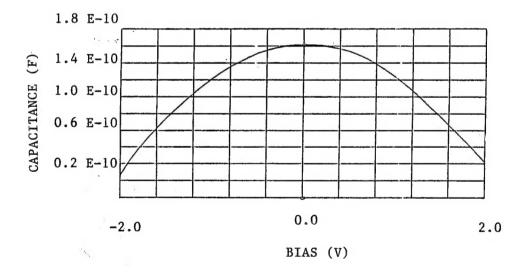


Fig. 2. Capacitance versus voltage for BSTO/1 wt% Oxide II deposited on $RuO_2/Sapphire$ with Pt top electrode.

TABLE I. Electronic Properties of BSTO (Ba = .6) and BSTO/Oxide Composite Thin Films.

<u>Material</u>	Applied Field (V/μm)		<u>ε'(V=0)</u>		% Tunability	
	<u>Film</u>	Bulk	<u>Film</u>	<u>Bulk</u>	<u>Film</u>	<u>Bulk</u>
BSTO	3.3	0.73	1380	3300	48	20
BSTO / OXIDE II	3.3	2.5	600	2700	34	46
BSTO / OXIDE III (Ref. 3)	2.0	2.3	398	1276	79	16

CONCLUSION

Thin films of both undoped and oxide modified BSTO have been deposited by PLD onto RuO₂/Sapphire substrates. The electronic properties of the undoped and oxide modified BSTO thin films exhibited similar trends relative to the bulk materials as shown in Table I.

We have shown that the tailoring of the electronic properties of BSTO thin films in the low frequency region is possible through the incorporation of metal oxides. The lowering of the dielectric constants, alongwith a high tunability, plays an important role in the impedance matching of these films into the electronic circuits. Further investigation of such tailoring in the microwave region through the incorporation of such oxides is underway.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Neville Sonnenburg of CPRL, M.I.T. for his help with GAXRD.

REFERENCES

- 1. L.C. Sengupta, S. Stowell, E. Ngo, M.E. O'Day and R. Lancto, *J. of Integrated Ferroelectrics*, (1994), in press.
- 2. R. Babbitt, T. Koscica, W. Drach, and D. Didomenico, J. of Integrated Ferroelectrics, (1994), in press.
- 3. S. Sengupta, L.C. Sengupta, S. Stowell, W.E. Kosik, E. Ngo, D.K. Vijay, and S.B. Desu, IEEE Transactions of the Proceedings of ISAF '94, Penn State, University Park, PA, (in press).
- 4. C.J. Brennan, Integrated Ferroelectrics 2, 73 (1992).

DISTRIBUTION LIST

	DISTRIBUTION LIST
No. of Copies	To
1	Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301
1	Director, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197 ATTN: AMSRL-OP-SD-TP, Technical Publishing Branch AMSRL-OP-SD-TA, Records Management Administrator
1	Director, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197 ATTN: Technical Library
2	Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 23304-6145 ATTN: DTIC-FDAC
1	MIA/CINDAS, Purdue University, 2595 Yeager Road, West Lafayette, IN 47905
1	Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709-2211 ATTN: Information Processing Office
1	Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333 ATTN: AMCSCI
.1	Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005 ATTN: AMXSY-MP, H. Cohen
1	Commander, U.S. Army Missile Command, Redstone Arsenal, AL 35809 ATTN: AMSMI-RD-CS-R/Doc
2	Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801 ATTN: Technical Library
1	Commander, U.S. Army Natick Research, Development and Engineering Center, Natick, MA 01760-5010 ATTN: DFAS-IN-EM-TL, Technical Library
1	Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703 ATTN: Technical Document Center
1	Commander, U.S. Army Tank-Automotive Command, Warren, MI 48397-5000 ATTN: AMSTA-ZSK AMSTA-TSL, Technical Library
1	Commander, White Sands Missile Range, NM 88002 ATTN: STEWS-WS-VT
1	President, Airborne, Electronics and Special Warfare Board, Fort Bragg, NC 28307

1 ATTN: Library

1

Director, U.S. Army Research Laboratory, Weapons Technology, Aberdeen Proving Ground, MD 21005-5066

1 ATTN: AMSRL-WT

Commander, Dugway Proving Ground, UT 84022

1 ATTN: Technical Library, Technical Information Division

Commander, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783 ATTN: AMSRL-SS

Director, Benet Weapons Laboratory, LCWSL, USA AMCCOM, Watervliet, NY 12189

ATTN: AMSMC-LCB-TL

1 AMSMC-LCB-R

AMSMC-LCB-RM

1 AMSMC-LCB-RP

Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E., Charlottesville, VA 22901-5396

3 ATTN: AIFRTC, Applied Technologies Branch, Gerald Schlesinger

Commander, U.S. Army Aeromedical Research Unit, P.O. Box 577, Fort Rucker, AL 36360 ATTN: Technical Library

U.S. Army Aviation Training Library, Fort Rucker, AL 36360

1 ATTN: Building 5906-5907

Commander, U.S. Army Agency for Aviation Safety, Fort Rucker, AL 36362

1 ATTN: Technical Library

Commander, Clarke Engineer School Library, 3202 Nebraska Ave., N, Fort Leonard Wood, MO 65473-5000

1 ATTN: Library

Commander, U.S. Army Engineer Waterways Experiment Station, P.O. Box 631, Vicksburg, MS 39180

1 ATTN: Research Center Library

Commandant, U.S. Army Quartermaster School, Fort Lee, VA 23801

1 ATTN: Quartermaster School Library

Naval Research Laboratory, Washington, DC 20375

2 ATTN: Dr. G. R. Yoder - Code 6384

Chief of Naval Research, Arlington, VA 22217

1 ATTN: Code 471

Commander, U.S. Air Force Wright Research & Development Center, Wright-Patterson Air Force Base, OH 45433-6523

1 ATTN: WRDC/MLLP, M. Forney, Jr.

1 WRDC/MLBC, Mr. Stanley Schulman

- U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899
- 1 ATTN: Stephen M. Hsu, Chief, Ceramics Division, Institute for Materials Science and Engineering
- 1 Committee on Marine Structures, Marine Board, National Research Council, 2101 Constitution Avenue, N.W., Washington, DC 20418
- Materials Sciences Corporation, Suite 250, 500 Office Center Drive, Fort Washington, PA 19034
- 1 Charles Stark Draper Laboratory, 555 Technology Square, Cambridge, MA 02139

Wyman-Gordon Company, P.O. Box 8001, North Grafton, MA 01536-8001

1 ATTN: Technical Library

General Dynamics, Convair Aerospace Division, P.O. Box 748, Fort Worth, TX 76101

1 ATTN: Mfg. Engineering Technical Library

Plastics Technical Evaluation Center, PLASTEC, ARDEC, Bldg. 355N, Picatinny Arsenal, NJ 07806-5000

- 1 ATTN: Harry Pebly
- 1 Department of the Army, Aerostructures Directorate, MS-266, U.S. Army Aviation R&T Activity AVSCOM, Langley Research Center, Hampton, VA 23665-5225
- 1 NASA Langley Research Center, Hampton, VA 23665-5225
 - U.S. Army Vehicle Propulsion Directorate, NASA Lewis Research Center, 2100 Brookpark Road, Cleveland, OH 44135-3191
- 1 ATTN: AMSRL-VP

Director, Defense Intelligence Agency, Washington, DC 20340-6053

- 1 ATTN: ODT-5A (Mr. Frank Jaeger)
 - U.S. Army Communications and Electronics Command, Fort Monmouth, NJ 07703
- 1 ATTN: Technical Library
 - U.S. Army Communications and Electronics Command, Intelligence and Electronic Warfare Center, Fort Monmouth, NJ 07703-5211
- 1 ATTN: Frank Elmer, AMSEL-RD-IEW-TAE-M
 - U.S. Army Research Laboratory, Electronic Power Sources Directorate, Fort Monmouth, NJ 07703
- 1 ATTN: AMSRL-EP-M, W. C. Drach
- 1 AMSRL-EP-M, T. E. Koscica
- 1 AMSRL-EP-M, R. W. Babbit

Director, U.S. Army Research Laboratory, Watertown, MA 02172-0001

- 2 ATTN: AMSRL-OP-WT-IS, Technical Library
- 25 Authors